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Research Article

Phase Transitions and Magnetocaloric Properties in $MnCo_{1-x}Zr_xGe$ Compounds

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The structural, magnetic, and magnetocaloric properties of $MnCo_{1-x}Zr_xGe$ ($0.01 \leq x \leq 0.04$) have been studied through X-ray diffraction, differential scanning calorimetry, and magnetization measurements. Results indicate that the partial substitution of Zr for Co in $MnCo_{1-x}Zr_xGe$ decreases the martensitic transition temperature (T_M). For $x = 0.02$, T_M was found to coincide with the ferromagnetic transition temperature (T_C) resulting in a first-order magnetostructural transition (MST). A further increase in zirconium concentration ($x = 0.04$) showed a single transition at T_C. The MST from the paramagnetic to ferromagnetic state results in magnetic entropy changes ($-\Delta S_M$) of 7.2 J/kgK for $\Delta H = 5$ T at 274 K for $x = 0.02$. The corresponding value of the relative cooling power (RCP) was found to be 266 J/kg for $\Delta H = 5$ T. The observed large value of MCE and RCP makes this system a promising material for magnetic cooling applications.

1. Introduction

The magnetocaloric effect (MCE) is a phenomenon in which a magnetic material heats up when a magnetic field is applied and cools down when the field is removed. In recent years, magnetic refrigeration based on the MCE has been considered as a possible ecofriendly and energy efficient cooling technology alternative to conventional vapor cycle refrigeration [1, 2]. Therefore, the developments of new materials that show large MCEs are essential. To date, the largest MCEs have been reported in materials such as $Gd_5Si_2Ge_2$ [3], MnFe(P,As) [4], $LaFe_{13-x}Si_x$ [5], NiMn(Ga,Sb,In) based Heusler alloys [6], and $MnAs_{1-x}Sb_x$ [7], which all show first-order crystallographic and magnetic phase transitions simultaneously, that is, magnetostructural transitions (MSTs). Hence, the exploration and study of the new materials that exhibit MSTs is important for applications and fundamental physics.

MnCoGe belongs to the family of ternary metallic compounds MM′X, where M and M′ are 3*d* transition metals and X is Si or Ge. Stoichiometric MnCoGe displays ferromagnetic (FM) properties below the Curie temperature ($T_C \sim 345$ K). In the paramagnetic (PM) region, the alloy transforms to a high-temperature, Ni_2In-type hexagonal structure (space group $P6_3/mmc$) from a low-temperature TiNiSi-type orthorhombic structure (space group Pnma) at $T_M \sim 650$ K [8]. If the structural transition temperature (T_M) shifts to coincide with T_C, a magnetostructural phase transition with a large change in magnetization can be expected and can lead to large MCE values. Previous studies indicate that changes in stoichiometry, chemical composition, or application of external pressure can result in concurrent magnetic and structural transitions and therefore may increase the magnitude of magnetic entropy change to show a large MCE [9–16]. In this work, we present results on the partial replacement of Co by Zr in the $MnCo_{1-x}Zr_xGe$ system, which exhibits a MST and a large MCE.

2. Experiment

Polycrystalline samples with compositions $0.01 \leq x \leq 0.04$ were prepared by arc-melting high purity elements (99.99%)

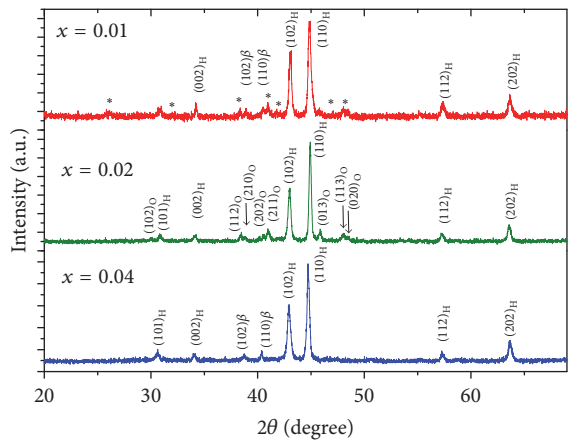

Figure 1: Room temperature XRD patterns of $MnCo_{1-x}Zr_xGe$ compounds with $0.01 \leq x \leq 0.04$. The orthorhombic and hexagonal peaks are indexed with *hkl* Miller indices with "O" and "H," respectively. The peaks indicated by "$*$" are unknown phase. The peaks labeled with *hkl* Miller indices with the symbol "β" are from the K_β wavelength, from the X-ray source.

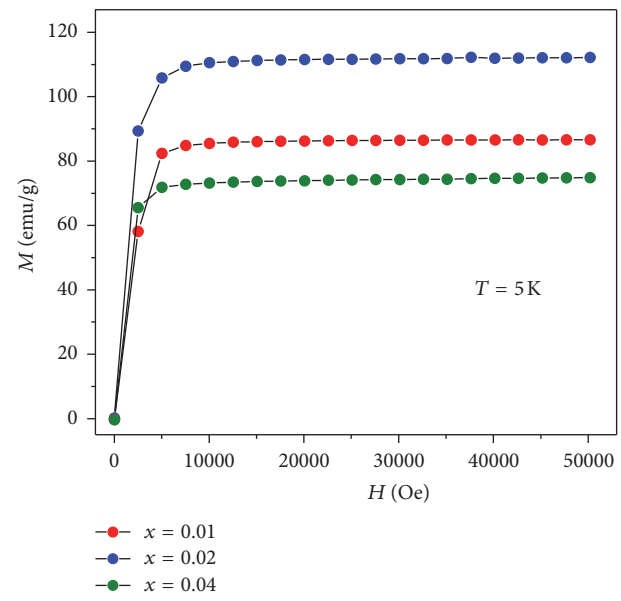

Figure 2: Field dependence of the magnetization $M(H)$ at $T = 5$ K.

in an ultrahigh purity argon atmosphere. The samples were turned over and remelted to ensure homogeneity. The crystal structures were determined by powder X-ray diffraction (XRD) using CuKα radiation at room temperature. A superconducting quantum interference device (SQUID by Quantum Design) magnetometer was used to measure the magnetic properties of the $MnCo_{1-x}Zr_xGe$ compounds in the temperature interval 5–380 K in applied magnetic fields up to 5 T. Differential scanning calorimetry (DSC) measurements were carried out using a DSC 8000 instrument (Perkin-Elmer) with a ramp rate of 30 K/min during heating and cooling in the temperature range 150–450 K to detect the temperature induced first-order transitions.

3. Results and Discussion

The room temperature XRD patterns of $MnCo_{1-x}Zr_xGe$ compounds are shown in Figure 1. The sample with $x = 0.01$ is in mixture state of the hexagonal (of about 80%) and unknown phase at room temperature. At Zr concentration, $x = 0.02$, the hexagonal (Ni_2In-type) structure stabilizes near room temperature with a small trace of orthorhombic phase (~15%). For $x = 0.04$, the compound crystallizes in a single-phase hexagonal Ni_2In-type structure. It has been reported that the orthorhombic phase of the MnCoGe system has smaller Co-Co separation [9]. Increasing the distance between the Co-atoms, either by creating Co vacancies or by substituting a larger element, stabilizes the hexagonal (Ni_2In-type) phase at lower temperature [9, 17]. Therefore, the partial substitution of Co ($R_{Co} = 1.252$ Å) by the larger Zr atoms ($R_{Zr} = 1.602$ Å) [18] in $MnCo_{1-x}Zr_xGe$ serves to stabilize the high-temperature austenite phase at lower temperatures.

Figure 2 shows the field dependence of the magnetization $M(H)$ at $T = 5$ K. The $M(H)$ curves at low temperature show that the compounds possess a ferromagnetic type of ordering in the ground state. The saturation magnetization (M_S) for the compound with $x = 0.02$ was found to be 3.72 μ_B/f.u., a value much larger than 2.87 μ_B/f.u. ($x = 0.01$) and 2.50 μ_B/f.u. ($x = 0.04$). It has been reported that the saturation magnetization of the parent MnCoGe in the orthorhombic structure ($M_S = 3.73\,\mu_B$/f.u.) is greater than that in the hexagonal structure (2.80 μ_B/f.u.) [19]. By comparing the saturation magnetization with that published in [19], and considering the results of the XRD and $M(T)$ measurements (Figures 1 and 3), we conclude that the compound with $x = 0.02$ is in the orthorhombic structure and that the samples with $x = 0.01$ and 0.04 are in the hexagonal phase, respectively, in the ground state. Therefore, the increase in saturation magnetization for $x = 0.02$ is attributed to the low-temperature FM orthorhombic phase.

The temperature dependence of the magnetization $M(T)$ of the compounds in an applied field of 100 Oe is shown in Figure 3. The $M(T)$ curves were measured during heating and cooling cycles within 10 K–380 K. The values of the Curie temperatures (T_C) were calculated from the minimum of dM/dT in the magnetization curve during the heating cycle (see inset of Figure 3). The $M(T)$ graph shows that the compounds are ferromagnetic at low temperatures. With increasing temperature, a large jump in magnetization was observed, which is typical for a FM to PM transition at T_C. A thermal hysteresis between heating and cooling curves was observed for the compound with $x = 0.02$ which is a signature of a first-order structural transformation at T_M. The first-order transition seen in the $M(T)$ curves for $x = 0.02$ was further confirmed by the observed endothermic and exothermic peaks in the DSC data (see Figure 4). Thus, a first-order MST from a FM TiNiSi-type phase to a PM Ni_2In-type phase is observed in $x = 0.02$ due to the coincidence of T_C and T_M. For the compounds with $x = 0.01$ and 0.04, a second-order magnetic transition (SOT) from a FM to PM state was observed. The calculated values of T_M and T_C are shown in Table 1.

Table 1: Transition temperatures, Curie-Weiss temperatures, saturation magnetization (M_S), effective magnetic moment, $-\Delta S_M^{\max}$, and RCP of $MnCo_{1-x}Zr_xGe$.

x	T_C (K)\$T_{M(DSC)}$ (K)	θ_P (K)	Ms (μ_B/f.u.) From $M(H)$	μ_{eff} (μ_B/f.u.)	Ms (μ_B/f.u.) From μ_{eff}	$-\Delta S_M^{\max}$ (J/kgK) H = 1 T\2 T\3 T\4 T\5 T	RCP (J/kg) H = 1 T\2 T\3 T\4 T\5 T
0.01	300\—	308	2.87	4.51	3.92	0.9\1.7\2.4\3.0\3.5	32\81\134\193\251
0.02	274\286	311	3.72	4.31	3.42	1.6\3.2\4.5\6.0\7.2	42\99\149\210\266
0.04	262\—	280	2.50	4.28	3.40	0.8\1.4\1.9\2.4\2.8	27\67\108\145\192

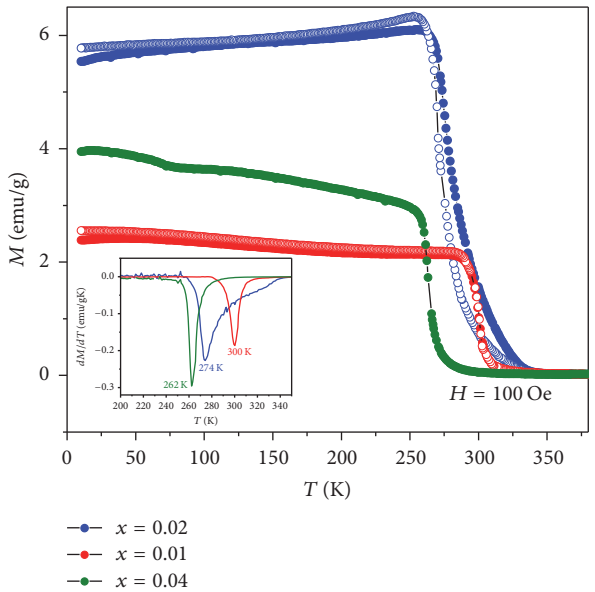

Figure 3: The temperature dependence of the magnetization $M(T)$ for $MnCo_{1-x}Zr_xGe$ with $0.01 \le x \le 0.04$ on heating and cooling in an applied field of 100 Oe. The solid and open symbols represent heating and cooling cycles, respectively. Inset: dM/dT versus T curves on heating.

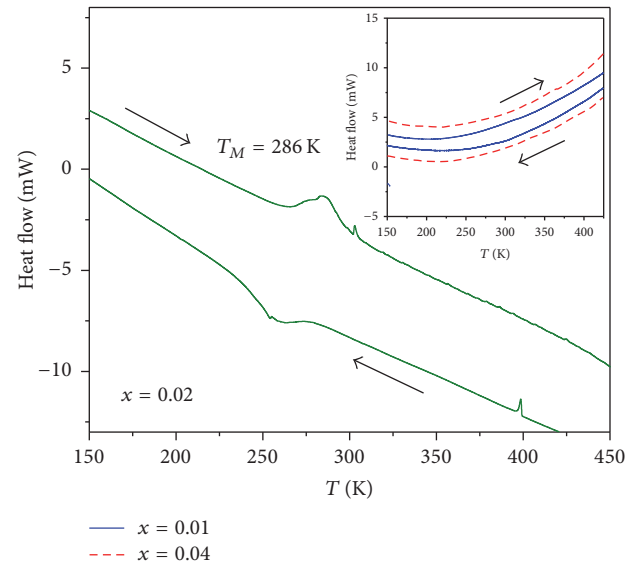

Figure 4: DSC heat flow curves (endothermic and exothermic peaks) as a function of temperature measured at the rate of 30 K/min during heating and cooling for the compound with $x = 0.02$. Inset: DSC heat flow curves for $x = 0.01$ and $x = 0.04$. The arrows indicate the heating and cooling cycles.

The temperature dependence of the inverse susceptibility $\chi^{-1}(T)$ for $MnCo_{1-x}Zr_xGe$ for $H = 100$ Oe is plotted in Figure 5. It is well known that the susceptibility (χ) follows the Curie-Weiss law, $\chi = C/(T - \theta_P)$, in the paramagnetic region, where C is the Curie constant and θ_P is the Curie-Weiss temperature. The values of the parameter θ_P were obtained by fitting the linear paramagnetic region and are given in Table 1. The observed values of θ_P are positive and larger than T_C, which indicates a ferromagnetic interaction between spins [20]. The effective magnetic moment (μ_{eff}) in the PM region has been calculated from $\chi^{-1}(T)$ data using the relation $\mu^2_{eff} = (3k_B/N\mu_B{}^2)C_m \approx 8\, C_m$, where $C_m = \chi T$ is the molar Curie constant [21]. The corresponding values of the saturation magnetization (M_S) were then calculated using $M_S = g \cdot J$ and $\mu_{eff} = g[J(J + 1)]^{1/2}$ [21]. The calculated values of μ_{eff} and M_S are listed in Table 1. Comparing the values of the saturation magnetization obtained from $M(H)$ and $M(T)$ curves (see Table 1), one can conclude that the orientation of the magnetic moments in the ground state of the compound in the orthorhombic structure ($x = 0.02$) is close to a parallel ferromagnetic type compared to

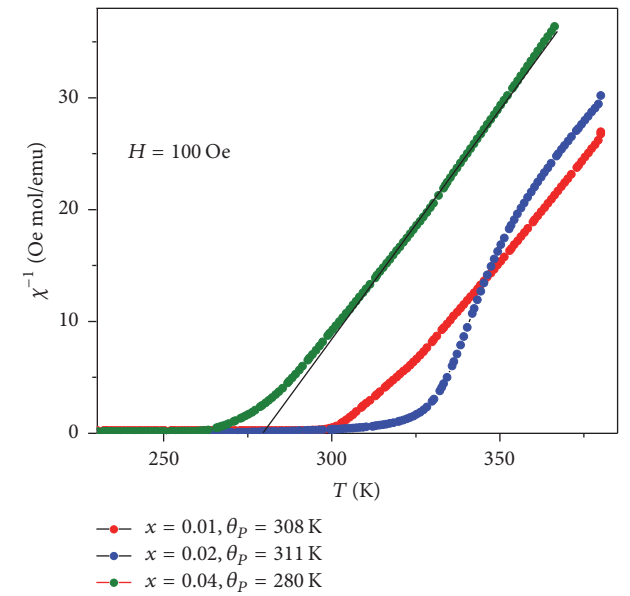

Figure 5: Temperature dependence of the inverse susceptibility in a field of 100 Oe. The solid line is the fitting according to the Curie-Weiss law.

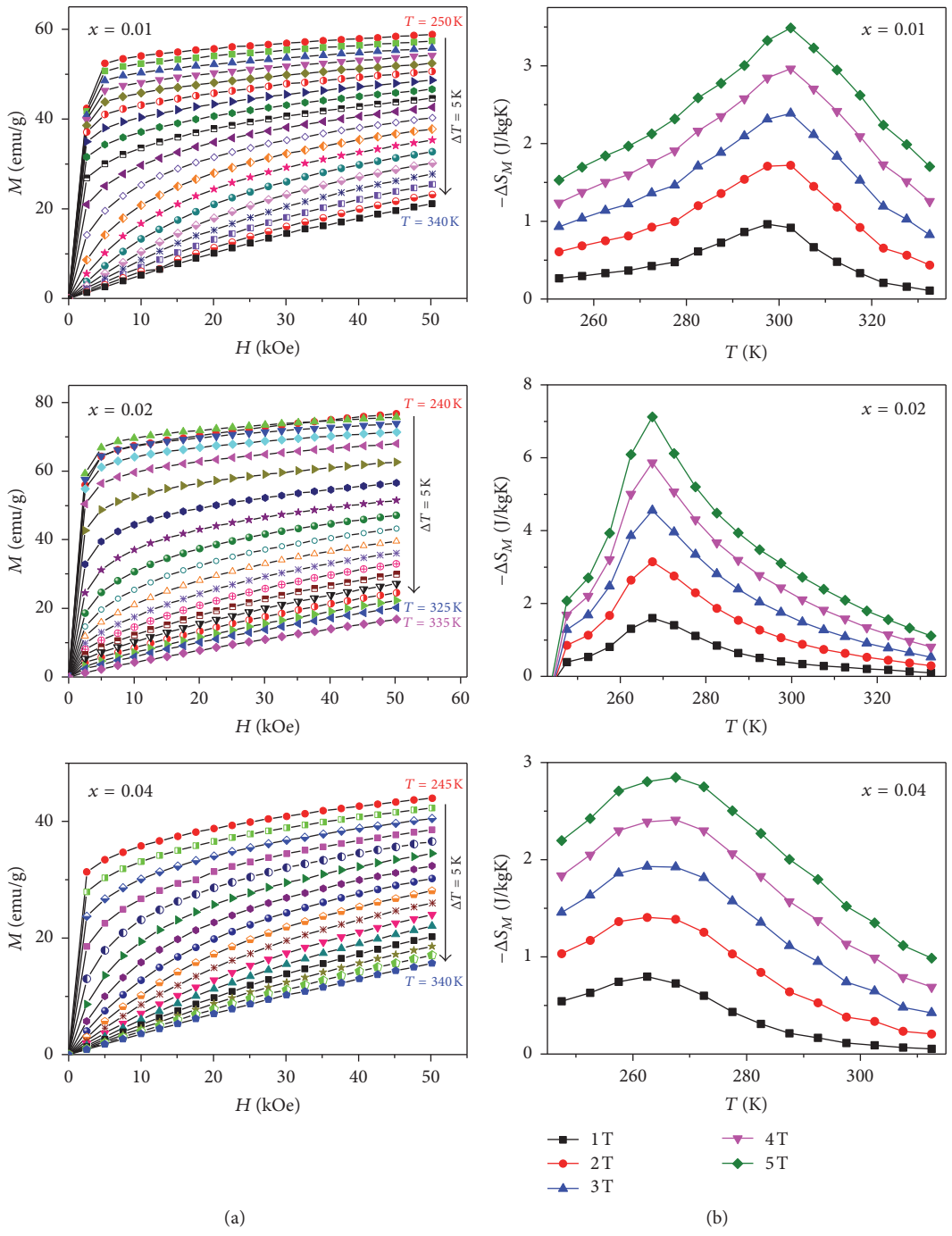

FIGURE 6: Isothermal magnetization $M(H)$ curves (a) and magnetic entropy changes, $-\Delta S_M(T)$ (b), with a magnetic field change $\Delta H = 5$ T for $MnCo_{1-x}Zr_xGe$.

a noncollinear ferromagnetic type in the compounds in the hexagonal structure ($x = 0.01, 0.04$).

The magnetic entropy change ($-\Delta S_M$) near the transition temperature for field changes up to 5 T is plotted in Figure 6. The $-\Delta S_M$ values were calculated from the isothermal magnetization curves $M(H)$ (shown in Figure 6) using the Maxwell relation, $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$ [1, 2]. The validity of the Maxwell relation to evaluate ΔS_M in the case of first-order transitions has been discussed in detail in [22]. A large $-\Delta S_M$ value of 7.2 J/kgK corresponding to a first-order magnetostructural transition was found for the compound with $x = 0.02$ for $\Delta H = 5$ T. The large value of $-\Delta S_M$ is attributed to the abrupt change in magnetization resulting from the coincidence of T_C and T_M brought forth by the Zr substitution for Co. For compounds with $x = 0.01$ and 0.04, smaller values of $-\Delta S_M$, 3.5 and 2.8 J/kgK, were found for $\Delta H = 5$ T, respectively.

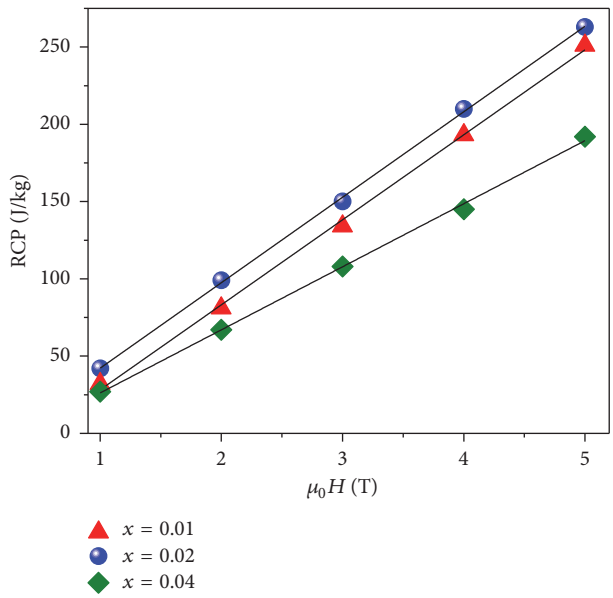

FIGURE 7: Field dependence of the RCP for $MnCo_{1-x}Zr_xGe$.

In addition to large magnetic entropy changes, large values of relative cooling power (RCP) are essential for magnetic refrigeration. RCP is an important parameter that estimates the usefulness of a material as a magnetic refrigerant. The RCP is a measure of amount of heat transferred between the hot and cold reservoirs in an ideal refrigeration cycle. It is defined as RCP = $-\Delta S_M$ (max) × δT_{FWHM}, where δT_{FWHM} is the full width at half maximum of the $-\Delta S_M$ curve [23]. The field dependence of the RCP for $MnCo_{1-x}Zr_xGe$ is shown in Figure 7. Large values of the RCP 251, 266, and 192 J/kg with ΔH = 5 T were found for x = 0.01, 0.02, and 0.04, respectively. The observed large values of $-\Delta S_M$ and RCP may be interesting for magnetic refrigeration applications.

4. Conclusions

The structural, magnetic, and magnetocaloric properties of $MnCo_{1-x}Zr_xGe$ compounds have been studied. Through the partial substitution of Zr for Co, the high-temperature austenite phase has been stabilized near room temperature. A first-order MST was observed for the composition with x = 0.02, resulting from the coincidence of T_C and T_M. Large values of $-\Delta S_M$ and RCP corresponding to first-order MSTs were observed for x = 0.02. Therefore, these large values of the magnetic entropy change and RCP and the nontoxic and less-expensive constituent elements make this system a promising material for magnetic cooling applications.

Conflicts of Interest

The authors declare no conflicts of interest in publication of this paper.

Acknowledgments

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